

NMR STUDY ON THE COMPATIBILITY OF ACR/PVC BLENDS

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ABSTRACT

A 300MHz solid NMR study on the compatibility of ACR (poly (methyl methacrylate-co-methacrylate), in the ratio of 1:1)-PVC (poly (vinyl chloride)) blends is reported. Spin-lattice (T_1) and spin-spin (T_2) relaxation time of ACR, PVC and their blends are recorded in the temperature range from 215K to 355K. Experimental results indicate that ACR and PVC are compatible with each other and the domain size is smaller than 25 nm, but heterogeneities of molecular dimensions still exist. Some problems of mechanism of compatibility and data analysis are also discussed.

The phase-separation on scales ranging from molecular dimensions to macroscopic dimensions of polymer blends, the degree of mixing achieved and the dimensions of phase domains of blends are the most important in the investigation of compatibility of blends. Pulsed NMR has provided useful information through the exploitation of (1) the short-range nature of the magnetic dipole-dipole interaction, which sensitively probes the nuclear environment on a scale of less than one nanometer, (2) an ability to delineate different morphological regions by virtue of their characteristic molecular relaxation, and (3) the transport of spin energy that may occur over tens of nanometers through the mechanism of spin diffusion. Compatibility of blends on these scales can be clearly explored. Pulsed NMR can give both qualitative and quantitative results, it is better than other methods. More recent studies using these methods are focused on some chemically dissimilar pairs of blends, for example: PVME/PS^[1], PVF₂/PMMA^[2], PSAN/PMMA^[3], PVC/PCL^[4], PVC/PMMA^[5] and so on.

In our study the ^1H spin-lattice relaxation time T_1 and spin-spin relaxation time T_2 of ACR (poly (methyl methacrylate-co-methacrylate), in ratio of 1:1), PVC (poly (vinyl chloride)) and their blends vs. temperature were recorded by pulsed NMR methods. The compatibility of this system is given and some problems of the compatibility mechanism and the data analysis are discussed.

Similar blends PMMA/PVC had been studied by DSC and solid NMR (30 MHz) methods. Schurer et al.^[6] suggested that the ester group was a proton-accepting group while the α -hydrogen of PVC was weakly proton-donating. This kind of dipole-dipole interaction makes the two polymers miscible. The NMR data^[5] showed that in the region of tens nanometers, the relaxation of $\alpha\text{-CH}_3$ in PMMA can relax the system and makes the blends compatible, but the compatibility of the blends in region of one or two nanometers is related to the relaxation of the ester group.

EXPERIMENTAL PART

1. Samples

ACR: $\bar{M}_n = 243000$. PVC: $\bar{M}_n = 52500$, $\bar{M}_w = 89300$.

(1) Blends Three ACR/PVC blends in composition of 25/75, 50/50, 75/25 by weight respectively were prepared. ACR and PVC were separately dissolved in THF and mixed according to the above proportions. Clear solutions were obtained after stirring for a long time. Samples of the blends were precipitated slowly with water, the precipitates were filtered and dried under vacuum at 10 mmHg, 313K to constant weights. (2) Mixtures The ACR/PVC physical mixtures of composition 25/75, 75/25 by weight were prepared by simply mixing two homopolymers together.

2. NMR Experiments

Solid ^1H T_1 (spin-lattice), T_2 (spin-spin) data were recorded on a Bruker MSL-300 spectrometer operating at proton resonant frequency of 300 MHz. The experimental temperature ranged from 215K to 355K and was controlled within ± 1 K. T_1 's were recorded by $(180^\circ - t - 90^\circ)$ pulse sequence, with 90° pulse of $2 \mu\text{s}$ duration. t was varied over a wide range to see if multiple T_1 components could be resolved. The analysis of T_1 decays which display more than one component had been reported by Wardell et al.^[7] T_2 's were recorded by solid echo $(90^\circ - t - 90^\circ)$ pulse sequence, and with $2 \mu\text{s}$ 90° pulse. T_2 values were computed from the free induction decays. The phase with smaller T_2 is denoted as T_{2s} phase and T_{2L} as the phase having longer T_2 . The methods of data analysis had been reported also^[8].

RESULTS AND DISCUSSION

T_1 , and T_2 data of ACR, PVC and their blends are shown in Fig.1, 2.

Solid NMR data at 30 MHz of PMMA and PVC had been reported^[5]. The T_1 vs. temperature plots had been examined. Since the frequency is 300MHz, the T_1 minima corresponding to T_g transitions of ACR and PVC in our experimental temperature range do not appear and they should move to higher temperature. There is a T_1 minimum of PVC at 300K that has not appeared in the plot reported earlier^[5]. We consider that this T_1 minimum correspond to the β -relaxation of PVC. The T_1 minimum of ACR near 300K corresponds to the onset of $\alpha\text{-CH}_3$ local motion. The main-chain torsional motion, which appears at higher temperature than $\alpha\text{-CH}_3$ on the T_1 vs. temperature

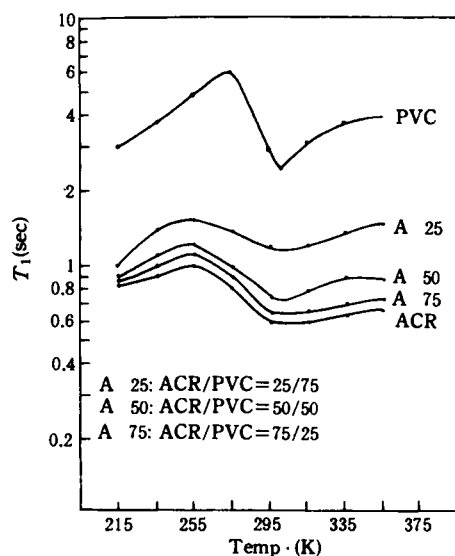


Fig.1 T_1 vs. Temp. plot (300MHz) of ACR, PVC and their blends

curve, is very near the $\alpha\text{-CH}_3$ T_1 minimum, so that the T_1 minimum near 300K is broad and shallow, unlike that of $\alpha\text{-CH}_3$ in PMMA (see [5]). The T_1 vs. temperature plots of ACR/PVC blends are similar to those of ACR. As the ratio of PVC in the blends increases, T_1 values increase while T_1 minima still stay at 300K.

There is spin diffusion between the heterogenous phases. It is possible through the mechanism of spin diffusion in the polymer blends the component that is tightly coupling to the lattice can relax other resonant nuclei either totally or partially. If this process is efficient and the spin-diffusion coupling is strong, spin energy can efficiently propagate through neighboring nuclei of the spin system, then a single T_1 value will be observed, and the system tends to be compatible. In the temperature region of experiment, a single T_1 of blends is observed in each case. But for the binary mixture, the plot shows two T_1 values which correspond to those of ACR and PVC respectively, and the ratio of the mixtures obtained from the data is the same as the composition (Fig.3). It implies that there is strong spin-diffusion coupling interaction between ACR and PVC in their blends, but not in their mixtures.

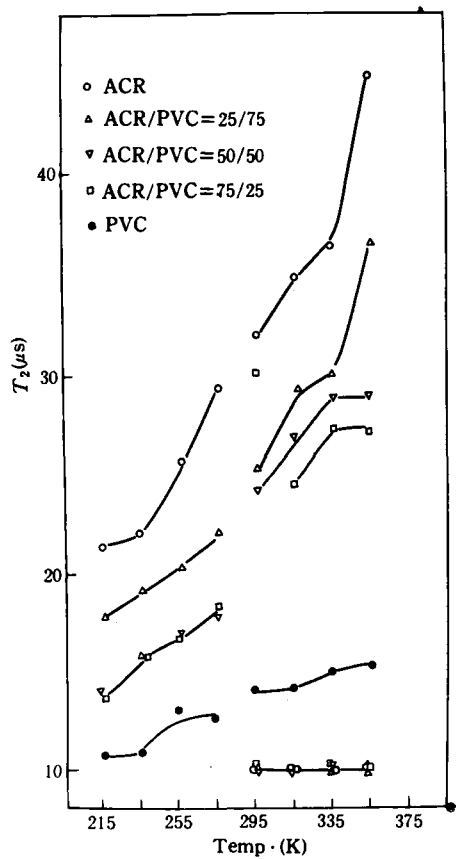


Fig.2 T_2 vs. Temp. plot of ACR, PVC and their blends. (300MHz)

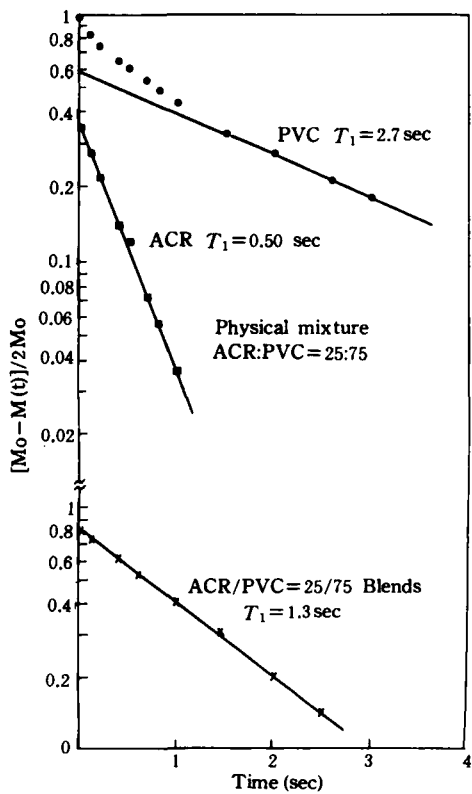


Fig.3 Comparison of T_1 of 25/75 physical mixture of ACR/PVC (■, ●) with T_1 of 25/75 ACR/PVC blends (×) at 300K

The root-mean-square diffusion path length is:

$$(r^2)^{1/2} = (6Dt)^{1/2}$$

(1)

where D is the diffusion coefficient, $= 10^{-12} \text{ cm}^2 \text{ sec.}^{-1}$, the time for diffusion $t = T_1$. Since T_1 s of the blends are about 1 sec., $(\tau^2)^{1/2} = 25 \text{ nm}$.

On the basis of strong spin-diffusion coupling, let $T_{1(1)}$, $T_{1(2)}$ and T_1 denote the observed spin-lattice relaxation time of N_1 , N_2 component and the total spin system respectively and N is the total number of protons in the blends. If M_1 , M_2 and M are the magnetization, then

$$dM/dt = T_{1(1)}^{-1} M_1 + T_{1(2)}^{-1} M_2 \tag{2}$$

and then:

$$T_1^{-1} = (N_1/N) T_{1(1)}^{-1} + (N_2/N) T_{1(2)}^{-1} \tag{3}$$

If W_1 is the weight fraction of component 1, A_1 and A_2 are the molecular weights of each mean structure unit containing n_1 , n_2 protons joining the total spin system, eq.(3) may be rewritten as follows:

$$\left(W_1 + \frac{A_1 n_2}{A_2 n_1 - A_1 n_2} \right) T_1^{-1} = W_1 \left(\frac{A_2 n_1}{A_2 n_1 - A_1 n_2} T_{1(1)}^{-1} - \frac{A_1 n_2}{A_2 n_1 - A_1 n_2} T_{1(2)}^{-1} \right) + \frac{A_1 n_2}{A_2 n_1 - A_1 n_2} T_{1(2)}^{-1} \tag{4}$$

For ACR(1)/PVC(2) system, $n_1 = 7$, $A_1 = 92.5$ and $n_2 = 3$, $A_2 = 63$, then

$$(W_1 + 1.7) T_1^{-1} = W_1 (2.7 T_{1(1)}^{-1} - 1.7 T_{1(2)}^{-1}) + 1.7 T_{1(2)}^{-1} \tag{5}$$

At the temperature higher than 300K, the $(W_1 + 1.7) T_1^{-1}$ vs. W_1 plots (as shown in Fig.4) are all linear, indicating that there is strong spin diffusion between ACR and PVC. Spin diffusion allows all of the blends to relax totally and no detectable number of protons exist in the blends at distances greater than 25 nm. We can say that ACR/PVC blends are intimately miscible and the domain size of the blends is less than 25 nm. Below 300K although a single exponential T_1 decay is also observed, the plots of $(W_1 + 1.7) T_1^{-1}$ vs. W_1 are not linear (shown in Fig.5). That can be easily understood. At 300K, α -CH₃ relaxation of ACR and β -relaxation of PVC appear simultaneously, these efficient relaxations are favourable for the blends to be compatible. Under higher temperature, in addition to the main-chain motion of ACR, the main chains segmental motion of the polymers renders the extent of chain entanglement more seriously, the interaction between two homopolymers is stronger

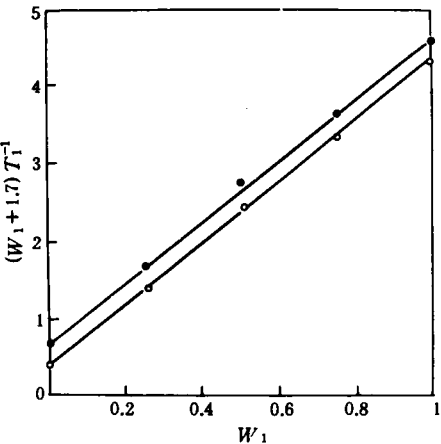


Fig.4 Plot of $(W_1 + 1.7) T_1^{-1}$ vs. W_1 for ACR/PVC blends at 300K (●) and 355K (○)

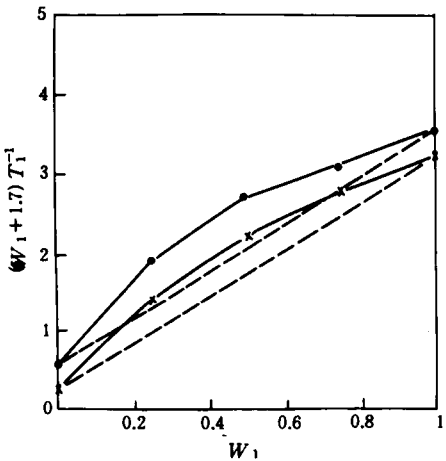


Fig.5 plot of $(W_1 + 1.7) T_1^{-1}$ vs. W_1 for ACR/PVC blends at 215K (●) and 275K (×)

than that at lower temperature and spin diffusion coupling is also stronger, certainly it is also beneficial for the blends to be miscible. The influence of β -relaxation of PVC on the compatibility of the blends in the distances determined by T_1 had not been mentioned in the previous work reported by others.

We have taken another way to analyse the data of our experiment. Since the multitransition of most homopolymers had been investigated by DSC, NMR, dielectric or dynamic mechanical methods, it is not very necessary to examine the relaxations of the blends first. On the basis of strong spin diffusion and under appropriate temperature, it is unnecessary to define the intrinsic relaxation rates of the relaxation sinks from the average T_1 values of the homopolymers observed in the experiment, put these intrinsic T_1 s, the numbers of the relaxation sinks' protons to eq.(3) to analyse the experiment data. We just consider the two homopolymers of the blends are the relaxation sinks. From our methods, we can observe the compatibility of polymer blends in the distances determined by the relaxation time just from the homopolymer structures of the blends, T_1 decays of the homopolymers and the blends at appropriate temperature.

At temperature below room temperature, the free induction decay of the blends can not be decomposed as it is difficult to distinguish the phases between the difference of T_{2s} and T_{2L} with small values. At higher temperature, phase-separation is clear and we can use the model of Gaussian and Lorentzian curve to fit the FIDs. The data of T_2 of ACR, PVC and their blends are shown in Fig.2. As the temperature increases, T_2 of T_{2s} phases do not change, but T_2 of T_{2L} phases increase significantly. It indicates that the blends are not completely miscible in molecular dimensions. The polymer chains of T_{2s} phases do not move easily as that of T_{2L} phases at room temperature. Even at higher temperature the T_{2s} phases are still very hard. But the ratio of T_{2L} phases increases as the temperature increases, especially when the ratio of one component is much higher than the other (Fig.6).

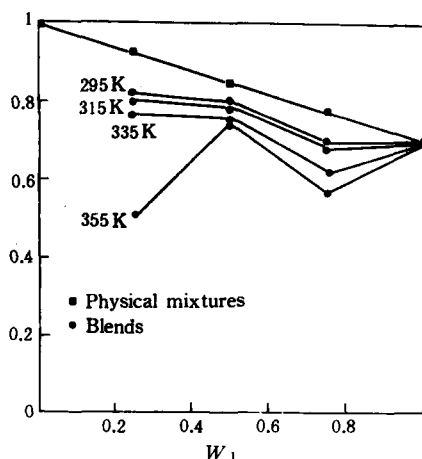


Fig.6 Plot of T_{2s} % vs. W_1 at 295K—355K for ACR/PVC blends and ACR/PVC physical mixtures

In summary, the NMR data presented in this paper indicate that ACR and PVC are compatible with each other and the domain size is smaller than 25 nm, but heterogeneities of molecular dimensions still exist.

Keywords:

Compatibility of polymer blends; solid NMR; ACR (poly (methyl methacrylate-co-methacrylate));

PVC (poly (vinyl chloride))

Acknowledgement We are grateful to Prof. He Manjun of East China Institute of Chemical Engineering for providing samples of ACR and PVC, and her helpful discussion.

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